Physics of DNAPL Migration and Remediation in the Presence of Heterogeneities

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Abstract

Spilled solvents have created pervasive groundwater contamination problems across the DOE complex because of their ubiquitous use, their toxicity and persistence in the environment, combined with the difficulty of recovering them from the subsurface. Because organic solvents are more dense than water and immiscible with water, they are commonly referred to as DNAPLs (dense non-aqueous phase liquids). They migrate below the water table downward and laterally under the influence of gravity, capillary, and viscous forces. Variations in media texture that the DNAPLs encounter as they migrate can have a profound influence on the migration path. This interplay between textural heterogeneities and driving forces complicates the migration of the DNAPLs and therefore it is not straightforward to predict the locations in the aquifer at which the spilled DNAPLs may ultimately reside. Uncertainties in the region of solvent contamination translate into higher remediation costs as the remedial system must be designed in light of these uncertainties. In an effort to clean up spilled DNAPLs, several remediation approaches are currently under development. Chemically enhanced solubilization, alcohol displacement, in situ oxidation, and air sparging are among the most promising. Many of these techniques have already undergone preliminary field demonstrations. However, results from such field demonstrations cannot be extrapolated to predict remedial performance under the wide range of field conditions to be encountered at spill sites across the DOE complex. Indeed, these techniques have not yet had the opportunity to be sufficiently tested and quantitatively compared in well-controlled laboratory experiments under heterogeneous conditions indicative of what can be expected in the field. In addition, the numerical simulation techniques used to predict DNAPL migration and remediation treatments have yet to be adequately verified through comparison against laboratory experiments conducted in heterogeneous media.

Our research effort funded by *EMSP* has been designed as broad and crosscutting. The goal of our research is to develop a fundamental quantitative understanding of the role of physical heterogeneities on DNAPL migration and remediation in aquifers. Such understanding is critical to cost effectively identify the location of the subsurface zone of contamination and design remediation schemes focused on removing the source of the contamination, the DNAPL itself. There are two major aspects to the DNAPL problem: finding them (migration) and cleaning them up (remediation). In an ambitious research plan, we have been working on both. By designing lab experiments within heterogeneous porous media analogous to field conditions, we have been able to directly observe DNAPL initial migration and subsequent interactions between injected remedial agents and the DNAPL. In these experiments we have identified critical mechanisms having important implications affecting both the initial migration and the successfulness of remedial processes.

For migration, we have found the influence of heterogeneities to yield high DNAPL saturation “pools” of a wide range of sizes, corresponding to the effects imposed by textural variations between geologic facies. These pools are interconnected by fingers where very little DNAPL resides. When viscous forces are low, we discovered the DNAPL structure to pulsate at both the pore scale within fingers and at the unit scale within large pools due to a capillary-gravity pulsation mechanism. We have built pore scale invasion mechanisms into a fundamentally new modeling approach, a form of Modified Invasion Percolation or MIP model. Our simulations yield results that closely track the migration behavior seen in our experiments. For remediation, we performed both micro-model experiments to elucidate surfactant enhanced mobilization and dissolution mechanisms as well as bench-scale remediation demonstration experiments for two different surfactants and an in situ oxidizer (potassium permanganate). From our results *we emphasize caution and advocate a restrained approach to site remediation at this time.* In all cases considered so far, the initial configuration of the DNAPL in pools and fingers dramatically influenced the efficacy of the remediation method.

Introduction

Chlorinated organic solvents have been used for many years as degreasers in industrial applications across the nation. Subsurface contamination resulting from the improper disposal of chlorinated organic solvents poses a significant yet unresolved remediation problem. Estimates by the EPA suggest that more than 50% of all sites on Superfund's national priority list are plagued by this class of subsurface contamination, commonly referred to as DNAPLs (dense non-aqueous phase liquids). The DOE and DOD have plenty of DNAPL problems as well. DNAPLs have been either confirmed or strongly suspected to exist as a separate liquid phase within underlying saturated zones at Rocky Flats, INEL, ORNL, Pinellas, Savannah River, Paducah, Portsmouth, Hanford, and most recently at Pantex.

There are several attributes of DNAPLs that makes this problem hard to crack:

- *DNAPLs are immiscible with water.* DNAPLs do not mix with water; they migrate as a separate phase. In multiphase systems capillary forces become important. Capillary forces vary spatially due to variations in sediment texture, thus complicating DNAPL migration behavior.
- *DNAPLs are denser than water.* DNAPLs can penetrate deep into aquifers making them much more difficult to find than light NAPLs which float on the water table. Remedial approaches seeking to enhance solubility also run the risk of reducing interfacial tensions sufficiently to induce downward mobilization. In one of our experiments (detailed below in accomplishments section) we have demonstrated catastrophic effects from inadvertent mobilization and have shown that currently accepted engineering practice is not sufficient to ensure against mobilization.
- *DNAPLs move funny.* The complex interplay of capillarity, textural heterogeneities, gravitational, and viscous forces governs DNAPL movement. Our experimental work clearly illustrates the intricacies of DNAPL migration. We graphically show that capillarity restricts the flow of the non-wetting phase to coarser regions where pore entry pressures are lower. Where these coarse regions form facies, lenses, or layers perpendicular to flow, there exists a lateral component to flow sufficient to outweigh the gravity forces causing downward migration. Once the facies either overflows or sufficient pressure is attained to penetrate into the underlying unit, DNAPL flows out of the facies again forming a finger and sinking deeper until yet another lens is encountered. This scenario is repeated over and over as the DNAPL migration progresses, filling coarse-textured facies while commonly bypassing the vast majority of the aquifer. Thus, the presence of coarse lenses serves to inhibit the downward migration of DNAPL and enhances the potential for lateral migration. At larger aquifer scales, this capillary effect often causes DNAPLs to move laterally in unforeseen directions causing considerable difficulty in locating DNAPL source regions. Variations in texture can have a profound effect on migration. At the majority of spill sites, we may never know enough geologic detail to use deterministic simulation approaches to aid in finding DNAPLs. It is this seeming unpredictability of DNAPL migration that makes them so difficult to find.
- *DNAPLs get stuck.* Capillary forces work to pin the phase in place leaving behind a residual saturation. They also reside in high saturation regions commonly referred to as "pools." These pools form as lenses that get bypassed during the DNAPL drainage process or as regions that exist in static equilibrium or at the advancing edge with insufficient head to overcome the entry pressure for further advance. Pools at the bottom of an aquifer are one example of this. (They don’t have enough head to break through confining layer beneath aquifer.) As aquifer and other subsurface sediments are heterogeneous from small to large scales, pools of many sizes will form. It is this DNAPL structure, residual and pooled DNAPL, that serves as the source region for dissolved-phase plumes. Plumes of contaminated groundwater emanate from these source regions as the DNAPL slowly dissolves over time into passing groundwater. It is because DNAPLs get stuck that pump and treat is so ineffective as a remedial process. It is an unfortunate irony that remedial processes that “unstick” the DNAPLs also lead to downward mobilization and

exacerbation rather than improvement of the problem. Our work has shown that DNAPL residing in pools must be explicitly considered in remedial design. Otherwise, unforeseen complications may arise.

Environmental research has traditionally progressed in a rather linear fashion in which basic science feeds more applied research, eventually leading to implementation. Oftentimes however, crosscutting activities and feedback loops can be used to identify and/or refocus promising research opportunities. In an era where investment in basic environmental research is believed to be underfunded (Washington Advisory Group, 1999), it is important to deploy research funds efficiently. We believe efficiency is served by including broad crosscutting research activities that can provide perspective and feedback as a complement to focused research activities dedicated to a specific important aspect of the problem. Our research effort funded by *EMSP* has been designed to this need. The goal of our research is to develop a fundamental quantitative understanding of the role of physical heterogeneities on DNAPL migration and remediation in aquifers. Such understanding is critical to cost effectively identify the location of the subsurface zone of contamination and design remediation schemes focused on removing the source of the contamination, the DNAPL itself. There are two major aspects to the DNAPL problem: finding them (migration) and cleaning them up (remediation). In a quite ambitious research plan, we have been working on both.

DNAPL Migration:

Lack of understanding and appropriate models for DNAPL migration hamstrings characterization and cleanup efforts because modeling provides an efficient means to integrate and synthesize characterization data with what we know about the physics of DNAPL migration. We need to bring to bear our improving understanding as to how DNAPLs migrate to help deploy characterization designed to locate DNAPL source zones. To do anything less is to pretend to know less than we do. The complexity of the DNAPL migration problem requires such integration. To fill this gap, in previous work we developed and implemented a Modified Invasion Percolation (MIP) model to simulate macro-scale DNAPL migration (Glass et al., 1995) for use in probabilistic delineation of DNAPL at field sites (Borchers et al., 1997a,b). Percolation models are considerably faster than standard multi-phase flow codes and therefore allow incorporation of more geologic detail. They also require different input parameters that are easier to obtain than those used in multi-phase flow codes. Such increased detail with more easily obtained parameters allows the textural changes within and across geologic units vital in the prediction of DNAPL migration to be honored. Because the underlying science was insufficient to support MIP application at field sites, we have designed and conducted a series of experiments to improve our understanding of migration physics that has supported model development. In our *EMSP* work, we have achieved great strides in improving the capability of MIP models. Our simulations yield results that closely track the migration behavior seen in our experiments with the DNAPL configured into fingers and pools corresponding to the effects imposed by the textural variations between geologic facies.

DNAPL Remediation:

In our *EMSP* work, we performed several first-of-a-kind, bench-scale remediation demonstration experiments. We found that two attributes of our work were of over-riding importance – representativeness and visualization. By building in geologically representative heterogeneities we were able to rely on natural migration processes to put DNAPLs in the right spots. That is, predominantly into pools. Making use of our quantitative visualization methods, we were able to observe interactions between DNAPLs, the heterogeneous flow field, and the remedial fluids and begin to understand processes that result from this interplay. Our well-controlled lab experiments allowed us to evaluate several promising remediation techniques under less idealized, more realistic conditions. By using our visualization methods, we are able to fully observe and quantify these interactions which can only (perhaps) be inferred using other (non-visual) experiments. In performing our experiments, we closely interacted with experts in each particular remedial process investigated. Our research results have provided some surprises. We expect the results of these demonstration experiments to help focus future basic research efforts directed toward DNAPL remediation.

In the remainder of this Interim Report, we first focus on our accomplishments over the period from August 1996 through August 2000. We then conclude with a summary and statement of "critical use results" for DOE DNAPL spill sites and cleanup efforts.

Accomplishments

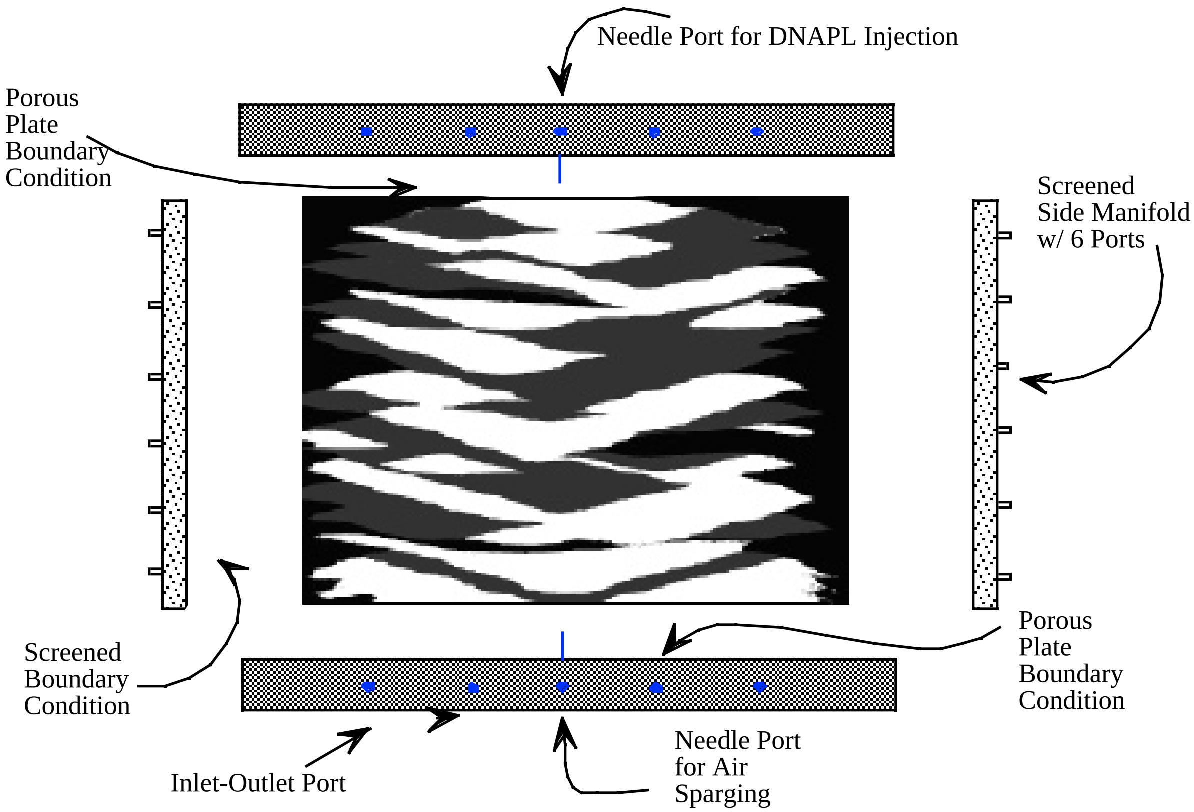
Our research objectives were to consider both the physics of migration and remediation in heterogeneous media. For migration, we had proposed to conduct a series of experiments against which to evaluate the validity of existing multi-phase flow theory as formulated in both percolation codes and in continuum flow codes. We expected that the experimental results would also provide new insights into DNAPL migration behavior. We believed that development of the invasion percolation model would provide an exciting alternative to continuum multi-phase flow codes. For remediation, we had proposed running a series of experiments to consider the efficacy of several promising DNAPL remediation techniques under realistic yet well-controlled conditions. We considered this work to be of the type of broad-based, initial studies needed to better understand the intricacies associated with various remedial processes. We expect that the results of this work will be used to focus subsequent research on those remedial approaches that appeared to offer the most promise. These objectives were broad and very ambitious. In the past three years we have made significant progress on both the migration and remediation aspects of the DNAPL problem as well as in the development of experimental and modeling capabilities required to accomplish our research objectives. Below we first cover general capability development (both in terms of experimentation and modeling) and then we outline the accomplishments for each of our two major thrusts, migration physics and remediation physics. In the process, we refer the reader to several journal articles where greater detail on many aspects of our results can be found.

Capability development:

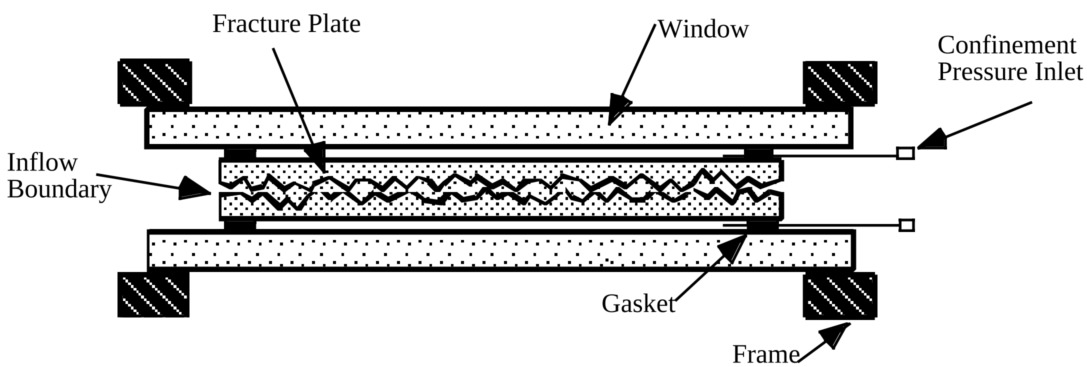
We started our *EMSP* funded research with a solid foundation in both experimental and modeling capabilities. Over the past there years, these capabilities have necessarily grown as we discovered new intricacies of both measurement techniques and DNAPL physics not previously included in our models. We outline these developments in the following sections.

Experimental Systems:

We have used both heterogeneous sand packs and micro-models in our experimental systems (see figure 1). Our heterogeneous sand packs have consisted of thin (1cm) but extensive (60x60cm) chambers filled with translucent sand where transmitted light visualization methods (e.g., Tidwell and Glass, 1994; Norton and Glass, 1993) are used to track phase and solute movement. The chambers are constructed such that boundary conditions can be tailored to suit the needs of a particular experiment. (That is, the edges of the chamber can be configured in a variety of ways, such as: flow, no flow, wetting, nonwetting, porous plates, screens, etc.). We have also used transparent micro-models and fractures (15x30 cm) to aid in our understanding of remediation physics. In these systems, our transmitted light visualization methods provide exquisite measurement resolution and accuracy for properties of interest such as, pore geometry (e.g., Detwiler et al 1999), phase structure and saturation (e.g., Nicholl and Glass, 1994; Nicholl et al. 2000), and solute concentration (e.g., Detwiler et al 2000). For these micro-model studies, we also built a special tipping light transmission setup (so that gravity could be varied) in our DNAPL lab where we have the proper environmental safety and health controls to use hazardous chemicals such as TCE. Our quantitative light transmission systems are controlled by computers that orchestrate a variety of functions simultaneously: 1) digital image acquisition using coupled charge device (CCD) cameras, 2) controlling pumping rates 3) the opening and closing of valves, 4) weighing of fluids entering or leaving the experiment, and 5) measuring fluid pressures. We have also reworked our systems to include a motorized insulating shutter to minimize the heat loading of an experiment from the light source. This shutter retracts automatically when a digital image is to be captured. Addition of the



a) Heterogeneous Sand Pack System, Plan View



b) Micro-model/Fracture system, Cross-section

Figure 1. Schematics of Experimental Systems: a) A heterogeneous sand pack 1 cm thick is held between two 3/4 - inch glass plates (see Glass et al., 2000; Conrad et al., *in review*). Chamber sizes used have been is 60 x 30 and 60 x 60 cm. Top and bottom manifolds are constructed of steel with inset porous plates. Porous plates distribute flow as well as maintain hydraulic connection during drainage. Side manifolds have six inter-connected ports to allow uniform fluid flow side to side. Fine screens provide the boundary conditions for the side manifolds, holding the sand but allowing easy transport of water, dyed water, remediation fluids, or DNAPL. Needles are provided at the top and bottom boundaries for injecting non-wetting fluids into the pack. **b)** A micro-model/fracture (15 x 30 cm) is created by forcing two pieces of rough glass plates together by confinement pressure yielding and mean aperture of 0.1 mm with a correlation length of 0.8 mm (see Nicholl and Glass, 1994; Zhong et al., 2001).

shutter is important in work with remediation fluids where solubility and emulsion formation are sensitive to temperature.

Creation of controlled heterogeneity:

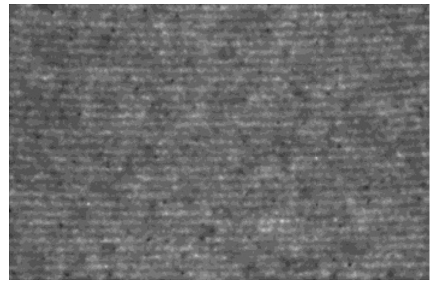
The heterogeneous sand packs we create must be representative of the natural subsurface environment while also allowing us to maintain experimental control. Continued development of our computer-controlled sand filler has allowed us to create reproducible heterogeneous sand packs. Using our unique packing technique allows us to vary system parameters from experiment to experiment (i.e., flow rate, interfacial tension, density, remedial fluids) while keeping the heterogeneous sand structure constant (i.e., reproducible). Our work initially considered structures similar to those seen in channel cut and fill deposits with facies-like macro-heterogeneities (see Glass et al 2000 and Conrad et al *in review* for details), but also has included some initial work with micro-layering. These small-scale laminations and cross-bedding features are ubiquitously found within individual facies of sedimentary deposits. In preparation for an assault on the influence of micro-layering on DNAPL migration, this past summer we revisited and greatly refined our methods for constructing micro-layers. We now have the ability to create micro-layered sands where the thickness and intensity of the variation across the interface can be varied systematically (see figure 2). As the tube supplying sand to the chamber traverses back and forth, grading occurs naturally as the sand hits the growing sand body to create a fine/course layer pair for each traverse. By widening the particle distribution of the parent sand, the intensity or property swing of the fine/course pair is increased; by decreasing the rate of the back and forth motion, the layers increase in thickness. In this way we are able to create micro-layering that grades naturally from fine to coarse, just as we find in natural deposits.

Measurement of sand pack and fluid properties:

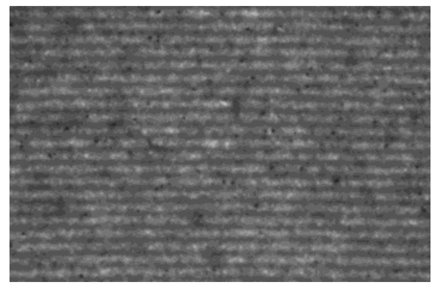
Characterization procedures have been developed to measure the permeability, relative permeability curves, and pressure saturation curves of each experimental sand. We found that these properties must be measured within the sand chamber where the sands are used. Measuring them in a standard ~5 cm diameter short column yields significantly different values due to the packing within the different geometries (our sand slab is 1 cm thick but 30 cm wide). We note that such geometric property forcing is interesting in their own right and has some significant implications with respect to taking samples, repacking them and measuring two phase flow properties for alluvial deposits. Image analysis capabilities have also been enhanced to yield better measurements of saturation within heterogeneous sand packs. While still of lower accuracy than application in homogenous fields, we are now achieving total mass balance for our heterogeneous systems of within 5%. We have also developed a combined theoretical/empirical approach to translate intensity fields using dry and fully saturated images to mean threshold radius at each point in the field for direct use our MIP modeling. Finally, we purchased a duNoy ring surface tensiometer to measure interfacial tensions between the immiscible fluid pairs used in our experiments; to analyze dissolved concentration of NAPL in effluent for the remediation experiments, we have purchased, tested, and used a gas chromatograph.

Modified Invasion Percolation (MIP) model development:

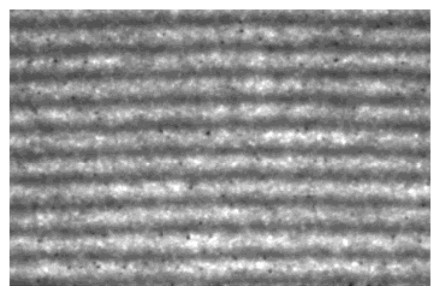
Our research previous to *EMSP* funding had indicated that porous continuum approaches would be hard pressed to appropriately represent the critical physics of DNAPL migration. In response, we had developed a rudimentary 3-D model based on Invasion Percolation, as introduced by Wilkenson and Willemson (1983). This model was modified and reconceptualized at a macro scale for use in delineating DNAPL migration in the field (Glass et al., 1995). Over the past three years and with leveraged funding from *EMSP*, *BES Geosciences* and *WIPP* where MIP is also being used, we have significantly enhanced the original model to apply to a wide range of problems in porous media



Thin micro-layers



Medium micro-layers



Thick micro-layers

Light zones are composed of coarser sand while dark are finer

Reproducable assembly of micro-layer types

30x60 cm chamber

Figure 2. Controlled Micro-layering Heterogeneity. We construct heterogeneous sand packs using our computer controlled sand-filler. Homogeneous, mixed parent sand is loaded into a cylindrical reservoir where it passes through screens at the bottom. It then falls into a funnel and down a tube into the chamber. The reservoir/funnel/tube can be located and relocated precisely as they are mounted on a computer controlled motion arm. By moving the assembly back and forth across the chamber we create a single naturally graded fine-coarse micro-layer pair: the faster the traverse, the thinner the layers; and the wider the distribution of grain sizes in the parent sand, the greater the layer intensity swing. Chambers can be filled with an entire single micro-layer type or with an assembly of types such as seen above on the left (note, the scale of all images are the same). We note that when we compare digital images, layers coincide to within ~3 mm and often better by the top of the chamber after filling its entirety.

and fractured rock. The code incorporates multiple neck pore filling facilitation for wetting invasion in porous media and gravity for different density fluids (Glass and Yarrington, 1996), in-plane curvature for fractures (Glass et al., 1998), and most recently, first order viscous forces (Glass et al., 2001). The code is 3-D and can accommodate up to 10^7 nodes (e.g., blocks, pores, or fracture apertures) on our current computers. In the context of work funded by *BES Geosciences*, the code is being combined with continuum models for phase dissolution and transport (Detwiler et al., *accepted*). We have also written an entirely new MIP code to incorporate the simultaneous invasion of both wetting and nonwetting fluids. A paper is currently in preparation (Glass and Yarrington, *in preparation*) that uses the new code to consider fragmentation and pulsation in three different systems where published experiments have shown it to occur: 1) gravity driven fingering of wetting fluids in initially dry media as studied by Glass et al (1989), 2) gravity driven fingering in fractures as presented by Nicholl et al. (1993, 1994), and 3) our DNAPL migration studies described below (Glass et al. 2000).

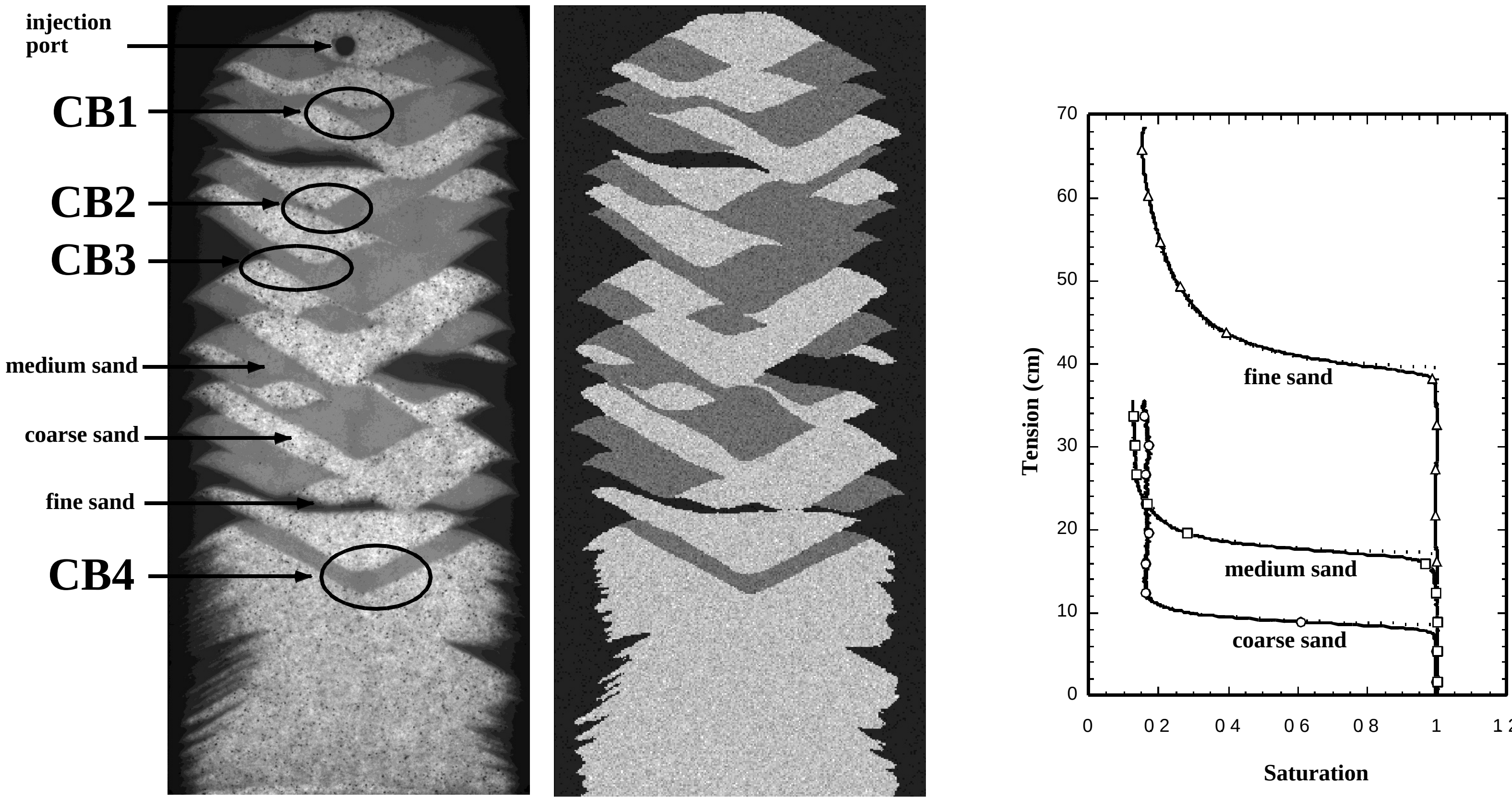
Migration Physics:

We began our study of DNAPL migration physics in simple macro-heterogeneous systems consisting of individual units that are essentially homogeneous within. Two papers cover this work: “Gravity-destabilized nonwetting phase invasion in macro-heterogeneous porous media: Experimental observations of invasion dynamics and scale analysis” (Glass et al., 2000), and “Gravity-destabilized nonwetting phase invasion in macro-heterogeneous porous media: Near pore scale macro modified invasion percolation simulation of experiments” (Glass et al., 2001). We then went on to consider on a preliminary basis the influence of viscous forces (flow rate) and capillary-gravity pulsation in macro-heterogeneous systems through a series of experiments and the development of the new model that includes the simultaneous wetting and nonwetting invasion (described above). We also began study of micro-layering heterogeneity with both preliminary experiments and simulations followed by the further development of our sand filling capability (described above) to allow the systematic exploration of this critical heterogeneity type. Below we briefly summarize each of these efforts in turn.

Macro-heterogeneous media: Experiments and Scale analysis

In Glass et al. (2000), we designed and conducted experiments in a heterogeneous sand pack where gravity-destabilized nonwetting phase invasion (CO_2 and TCE) could be recorded using our high resolution light transmission methods. The heterogeneity structure was designed to be reminiscent of fluvial channel lag cut-and-fill architecture and it contained a series of capillary barriers. As invasion progressed, nonwetting phase structure developed a series of pore scale fingers and macroscopic pools; behind the growing front we found nonwetting phase saturation to pulsate in certain regions when viscous forces were low (see figures 3, 4, and 5, note that this representation of invasion order blurs the pore scale nature of the invasion structure). This dynamic is due to the combination of gravitational forces and hysteretic capillary forces with viscous forces working to suppress pulsation as flow rate increases. To our knowledge, this is the first time such capillary-gravity pulsation dynamics have been clearly observed and explained and its repercussion for predictability is as yet unclear.

Through a scale analysis, we derived a series of length scales that describe finger diameter, pool height and width, and regions where pulsation occurs within a heterogeneous porous medium. In all cases, we found that the intrinsic pore scale nature of the invasion process must be incorporated into our analysis to explain experimental results. For instance, maximum pool height during migration is elevated significantly when viscous forces are important (under higher flow rates) because the pore scale finger structure within the capillary barrier increases viscous losses there. This



a) Experimental hetero-structure

b) Representative R field simulation

c) Drainage curve data and simulation

Figure 3. Digital image of the 60 cm tall macro- heterogeneous sand pack, simulation of R field and unit drainage curves: a) Digital image of the heterogeneous sand pack used in the invasion experiments. In this image the coarse sand transmits the most light and hence is the lightest; the medium sand appears gray; and the fine sand appears dark. The injection port and four major capillary barriers (labeled CB1 through CB4) are identified. These capillary barriers occur where medium sand separates coarse sand units. b) Representative R field simulation using unit locations and CDFs built from drainage curves measured on each unit. c) Comparison of measured and simulated drainage curves for each unit (solid lines designate data and dashed simulations). From Glass et al. (2000, 2001).

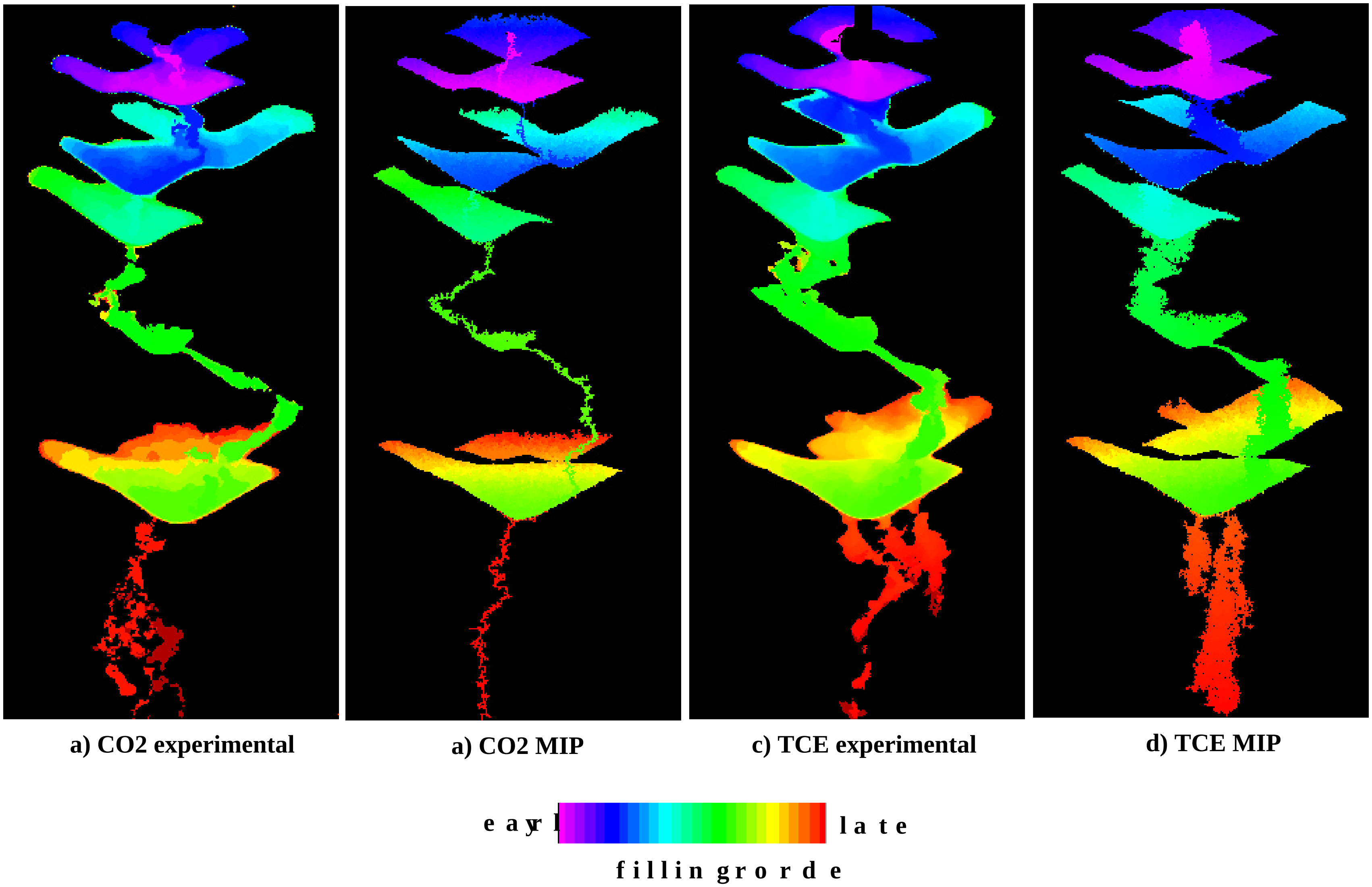


Figure 4. Invasion order images for experiments and MIP simulations: a) CO2 experiment, b) CO2 MIP simulation with no viscous forces, c) TCE experiment, d) TCE MIP simulation with viscous forces included. Colors represent first arrival filling order integrated across the thickness of the chamber or simulation network. CO2 experiments were conducted with chamber inverted (gas moving upward). Note that light refraction at the edges of the units and image reduction methods to yield first arrivial blurr the experimental images somewhat. MIP images look closer to what one can see in the experiment and reflect the pore scale detail very well. From Glass et al. (2000, 2001).

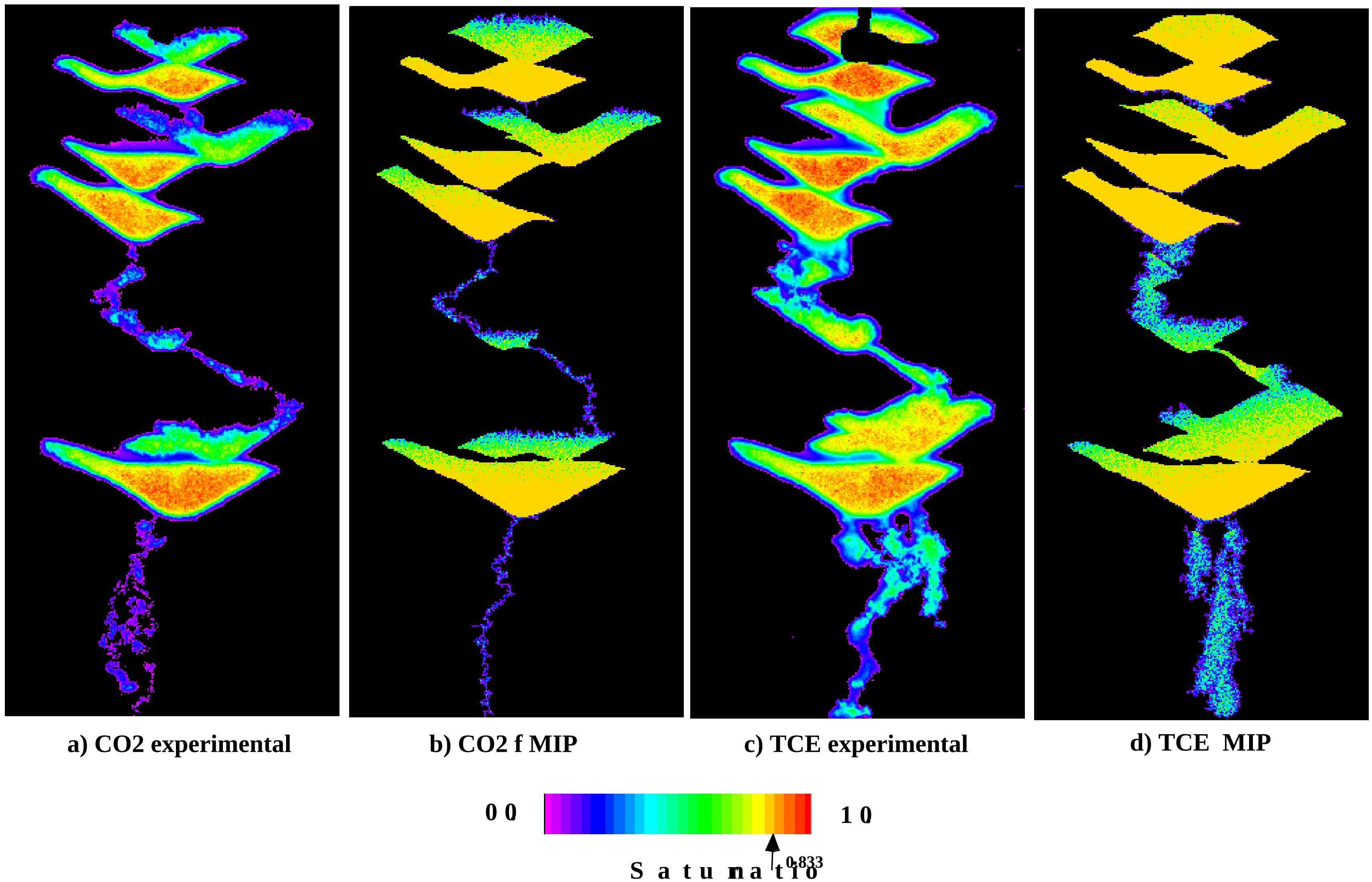


Figure 5. 2D saturation fields at system breakthrough: a) CO2 experiment, b) CO2 MIP simulation with no viscous forces, c) TCE experiment, d) TCE MIP simulation with viscous forces included. Colors represent non-wetting saturation averaged across the thickness of the chamber or simulation network, saturation of the non-wetting phase when the wetting phase is at residual (0.833) is noted on the color bar. Total volume of invaded fluid in MIP simulation matches experimental values for both CO2 and TCE of 51 and 73 ml, respectively. From Glass et al. (2000, 2001).

of course, places considerable constraints on the use of porous continuum approaches to conceptualize DNAPL migration. As an alternative at large scales, we proposed a simple macro-scale, structural growth model that assembles length scales for sub-structures to delineate nonwetting phase migration from a source into a heterogeneous domain. This model is akin to macro MIP but a step beyond in conceptual abstraction. For such a model applied to field scale DNAPL migration, we expect capillary and gravity forces within the complex subsurface lithology to play the primary roles with viscous forces forming a perturbation on the inviscid phase structure.

The implications of this study are far reaching and we urge the reviewer to read the concluding remarks in our paper. One of these we choose to emphasize here is that our experiments show most of the DNAPL is held in high saturation regions or “pools” caused by textural heterogeneity and very little is at the residual value as typically assumed. The difference between permeabilities at our barriers was only a factor of ~5, well within the range expected in natural aquifers. As heterogeneities within an aquifer are found at all scales, pools likewise will be found of all sizes. We point out that experiments and analyses founded on an assumption of nonwetting phase held predominantly as a residual saturation will have limited applicability to situations where mass is held predominantly in pools. Failure to consider the presence of DNAPLs held in pools during remediation design can lead to decreased performance or inadvertent downward mobilization. For example, in designing a surfactant flood to enhance aqueous solubility, using the results of laboratory column studies or trapping number calculations based on the assumption of residual saturation may significantly underestimate the potential for DNAPL mobilization of (as we will see in our remediation experiments below).

Macro-heterogeneous media: MIP model simulations

In Glass et al. (2001), we reconceptualized MIP at the near pore scale and apply it to simulate the non-wetting phase invasion experiments of Glass et al. (2000). For experiments where viscous forces were non-negligible, we redefine the total pore filling pressure to include viscous losses within the invading phase as well as the viscous influence to decrease randomness imposed by capillary forces at the front. MIP exhibits the complex invasion order seen experimentally with characteristic alternations between periods of gravity stabilized and destabilized invasion growth controlled by capillary barriers. The breaching of these barriers and subsequent pore scale fingering of the non-wetting phase is represented extremely well as is the saturation field evolution, and total volume invaded (see figures 3, 4, and 5). We note that this is a monumental success as it is highly unlikely that porous continuum approaches could model and match our experiment. Our current implementation of viscous effects has been accomplished in an effective sense for the entire field and is therefore only a first order implementation. Full implementation outlined in Glass et al. (2001) is based on the scale analyses presented in Glass et al. (2000), and requires understanding and incorporation of the role of viscous forces at the pore scale as the invasion process evolves. General model application requires such full implementation along with additional experimental validation.

Macro-heterogeneous media: Preliminary study of viscous forces and pulsation

In work described above (Glass et al. 2000, 2001), we found viscous forces to create multiple fingers as well as increase pool height above capillary barriers and thereby increase the probability of both breaking through and spilling over the barrier. Additionally, we discovered that the invading phase pulsates at both the pore and unit scales as viscous forces decrease. Because both viscous forces and capillary-gravity pulsation may lead to multiple pathway formation, we began to study these influences with both experimental and numerical approaches in macro-heterogeneous media. Our preliminary experiments in a macro-heterogeneous structure (identical to that shown in figures 3, 4, and 5) have used upward migration of CO_2 in a CO_2/water system as an analog for the downward migration of TCE as CO_2 could be dissolved away between tests. (Note, we ran a single test with TCE

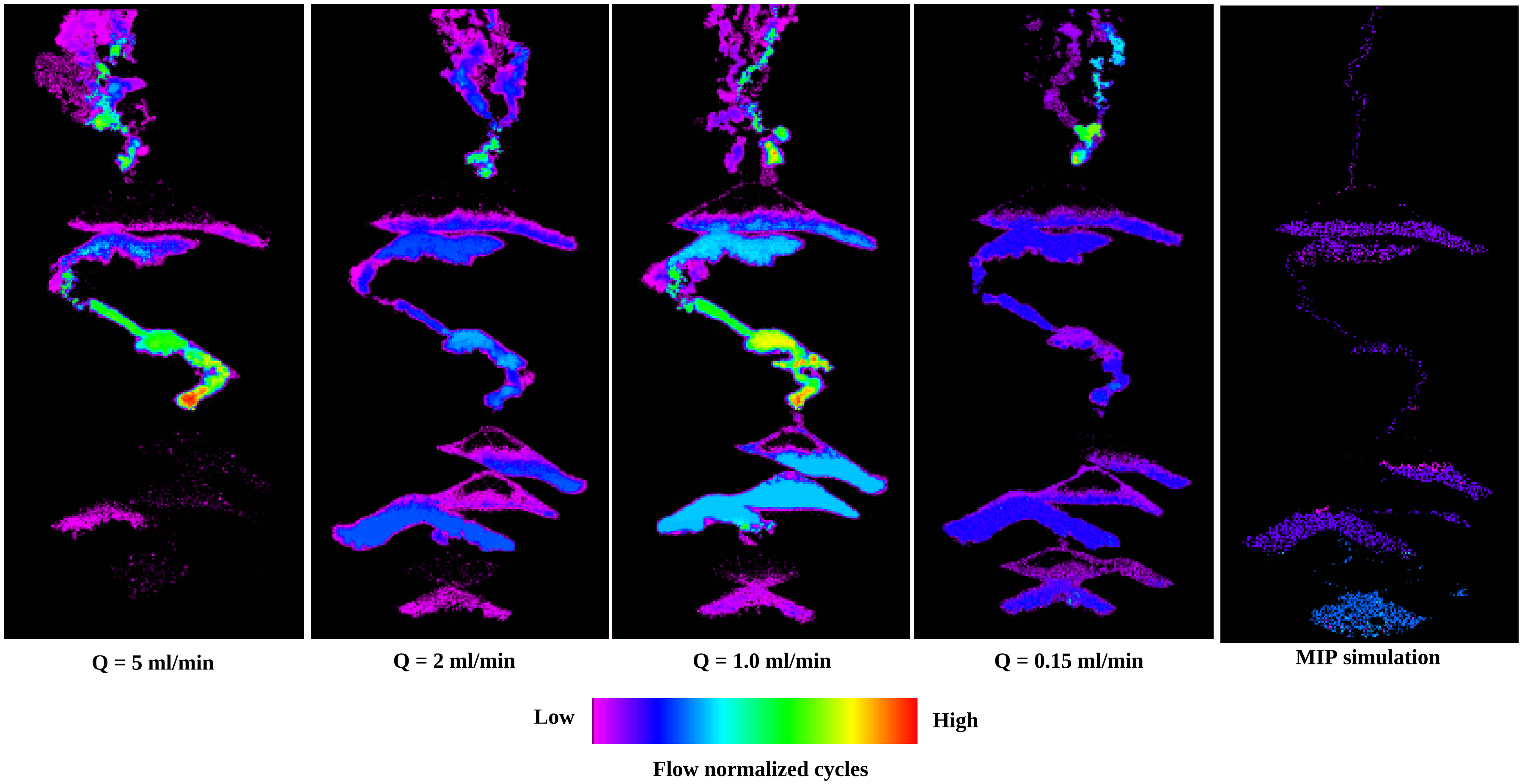


Figure 6. Capillary-gravity pulsation and suppression by viscous forces. The macro heterogeneous structure seen in figures 3 through 5 has been inverted and CO2 injected from below. After system breakthrough, images were gathered in time and pulsation cycles were counted as a function of location within the system. Flow rate normalized cycles is seen to vary within the flow structure as a function of flow rate. At 5 ml/minute, pulsation has been largely suppressed in the lower 1/3 of the cell. A MIP simulation with simultaneous wetting and nonwetting invasion neglecting viscous forces is shown at the right to yield very similar behavior as we see experimentally at low flow. Note however, we see higher pulsation near the source than in the experiment and also, we do not find the generation of multiple pathways below the final capillary barrier in the model as we see in the experiment.

as the invader to put to rest compressibility concerns.) Flow rate was increased through the range of our available equipment (from 0.1 ml/min. through 5 ml per minute) and data processed to consider the pulsation dynamics (see figure 6). Preliminary simulation with the new MIP model that includes simultaneous wetting and nonwetting invasion (described above) has recently been conducted. An example simulation is also shown in figure 6. We see that our model demonstrates pulsation at both the pore and unit scale as we see experimentally. Additional simulations where first order viscous effects have been included show the model to do a reasonable job in reproducing the trends we see in the experiment. However, full implementation of viscous forces as outlined in Glass et al. (2001) is required to complete this study. In addition, pulsation induced randomness independent of viscous forces must be included in the model to obtain the multiple pathways seen in the experiment. Based on results to date, we must recognize that both viscous forces and capillary-gravity pulsation have the potential to lead to multiple pathway formation and thus may influence the large scale migration structure. Such results, if proven to be general, may need to be incorporated into DNAPL migration models.

Preliminary study of Micro-layer heterogeneity:

In nearly every sedimentary deposit found in nature, micro-layering within individual units is ubiquitous. This heterogeneity within the macro-facies level structure may have a profound influence on DNAPL migration. We have begun considering the influence of micro-layering intensity in two preliminary experiments. Two different sands were used to increase micro-layering intensity while keeping thickness and orientation approximately the same. Results for invasion of CO_2 from a point source at the bottom of the pack are shown in figure 7. As can be seen, the influence of micro-layering intensity is quite important in defining the migration structure. We also note that capillary-gravity pulsation led to the bifurcation of the migration pathway 3 times over the course of the experiment. Example simulations for these experiments without simultaneous wetting and nonwetting invasion are also shown in the figure and are seen to capture the essence of the migration behavior. In order to accomplish such simulation we have used a mapping from transmitted light images to threshold pore radius fields (discussed above). Based on these encouraging results, we went back to refine our methods for creating micro-layered sand structures. We now can create experimental structures where both the micro-layer intensity and layer thickness can be varied systematically with exceptional reproducibility (discussed above) and are now ready for systematic experimentation and simulation.

Remediation Physics:

We began our study of DNAPL remediation physics with a study at the micro-scale and then designed and conducted a suite of experiments within a large sand slab cell (60x60x1 cm) containing macro-heterogeneities. Two papers cover this work: “Visualization of surfactant enhanced NAPL mobilization and solubilization in a two-dimensional micro-model” (Zhong et al., 2001), and “Bench scale visualization experiments of DNAPL remediation processes in an analog heterogeneous aquifer: surfactant floods and in situ oxidation using permanganate” (Conrad et al, *in review*), can be found in the Appendix. We have also conducted a preliminary partitioning interwell tracer test (PITT) with provocative results. We briefly summarize this work below and end with some thoughts on remediation modeling.

Micro-model study of surfactant mobilization and dissolution:

In Zhong et al. (2001) we teamed with colleagues at Michigan Tech (their funding originated from *EPA*) who were actively studying surfactant remediation techniques. We used a two-dimensional

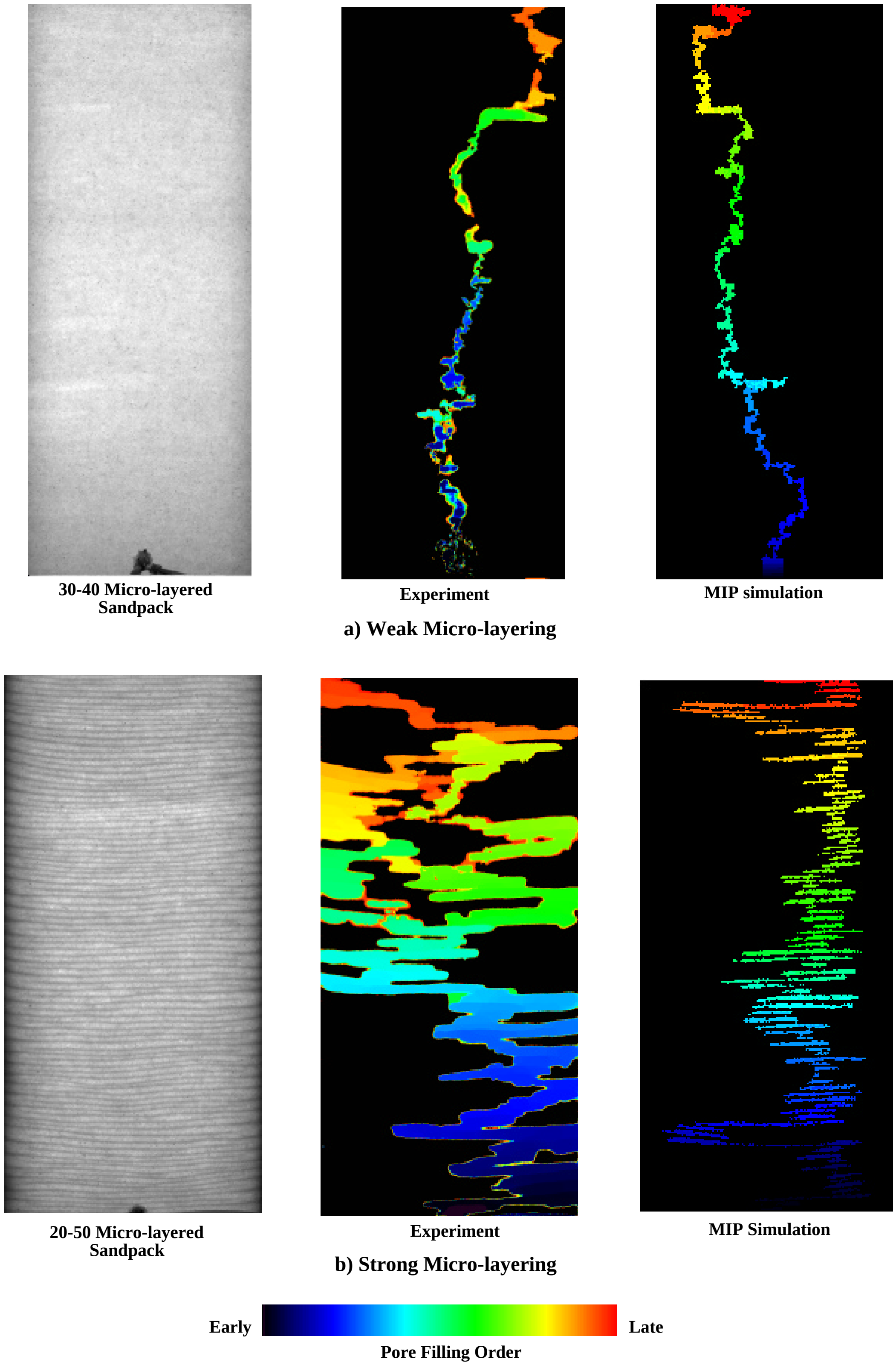


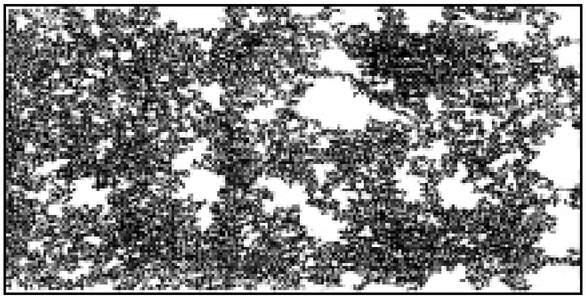
Figure 7. Influence of Micro-layering on nonwetting phase migration: Preliminary experiments and MIP simulations were conducted in microlayered sands 60 cm tall with a) weak and b) strong intensities. Colors represent first arrival filling order integrated across the thickness of the chamber or simulation network. Light refraction at the micro-layers and image reduction methods to yield first arrival blurr the experimental images somewhat. MIP images look closer to what one can see in the experiment and reflect the pore scale detail seen in the experiments extremely well. Also note that strong multiple pathways have formed in the strong micro-layer experiment due to gravity-capillary pulsation.

pore network (or fracture) and our quantitative visualization system to observe surfactant-enhanced NAPL mobilization and solubilization phenomena at the micro-scale. The micro-model consisted of two plates of textured glass held in contact, producing a series of variably-sized, connected apertures available for fluid flow. The quantitative visualization system was capable of resolving micro-model aperture geometry and the evolution of NAPL phase structure and saturation. For each experiment, a common residual NAPL field was established with a NAPL flood into the water saturated micro-model followed by a water flood at low flow rates. We then conducted a series of mobilization/solubilization experiments where the chemical formulation of the flood was varied from pure water to floods containing an anionic surfactant (MA) and co-solvent (alcohol) at fixed concentrations and a range of electrolyte (NaCl) concentrations. The variations in the electrolyte concentrations provided a range of IFTs and NAPL solubilities. For the surfactant floods, the flow rate was kept at the same rate used to establish the residual NAPL, yielding a final N_{ca} (capillary number) modified only by changes in the IFT. For the pure water floods, the flow rate was varied to modify the N_{ca} by changes in viscous forces alone (see figure 8).

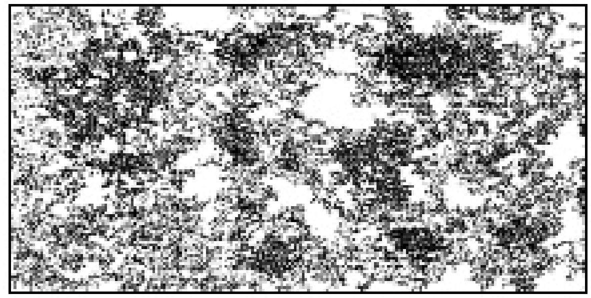
When $N_{ca} < 10^{-3}$, for a given N_{ca} we found significant differences in the macro-scale saturation at the end of the mobilization stage of the experiments. The observed differences occur because the changes in the local N_{ca} during the surfactant floods occurs through a miscible displacement process, while during pure water floods, changes in the local N_{ca} are established immediately throughout the field. This path dependency, i.e., changes in the local N_{ca} via increases in viscous forces or via miscible IFT reduction, is in turn caused by differences in micro-scale processes. For the surfactant floods, a high NAPL saturation front forms normal to the direction of flow and sweeps the entire field width. The IFT reduction fronts form due to the combination of N_{ca} induced downstream and capillary-driven upstream mobilization processes. For the water floods, rivulets oriented in the direction of flow form and are driven downstream. Rivulet formation occurs through the simultaneous application of viscous forces in primarily a single direction throughout the field. These very different, path-dependent, micro-scale processes between the surfactant and pure-water floods lead to a difference in final macro-scale saturation. The differences in saturation are attributed to differences in the number of remaining, entrapped NAPL blobs, rather than differences in final blob size statistics.

Solubilization of the residual NAPL remaining after the mobilization stage was dominated by the formation of dissolution fingers (see figure 8). The fingers developed and propagated faster at lower residual NAPL saturations and when the aqueous phase solubility was higher. The location of finger initiation and propagation was directly related to spatial heterogeneity in the aperture field. Equilibrium NAPL mass removal rates were observed before the dissolution fingers broke through the effluent edge of the micro-model. Following finger breakthrough, the solubilization rate decreased below the rate expected if equilibrium solubilization were occurring throughout the micro-model and continued to decline as the back of the dissolution finger zone advanced to the downstream boundary. Thus, at the flow rates and chemical formulations considered in our experiments, macro-scale non-equilibrium NAPL solubilization can be attributed directly to the development of a dissolution finger zone where significant heterogeneity occurs due to micro-scale dissolution fingering.

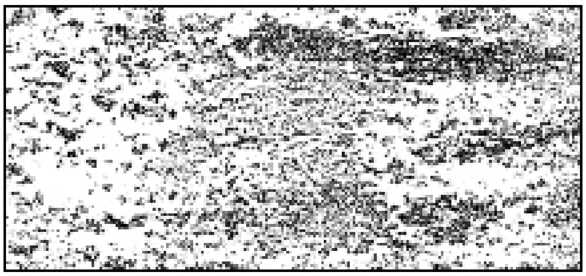
A macroemulsion phase was also observed to form spontaneously and persist during portions of the solubilization stage of the experiments (see figure 8). The occurrence of the macroemulsion was related directly to local NAPL saturation, where macroemulsion formation was found to be more likely at higher local NAPL saturations, and was at least indirectly related to electrolyte concentration in the surfactant formulation. The impact of macroemulsion on solubilization rates is unclear, since micro-model effluent concentrations and aqueous phase flow patterns did not appear to be affected by macroemulsion occurrence.



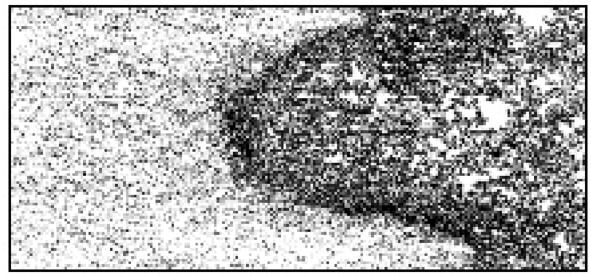
a) TCE after primary invasion



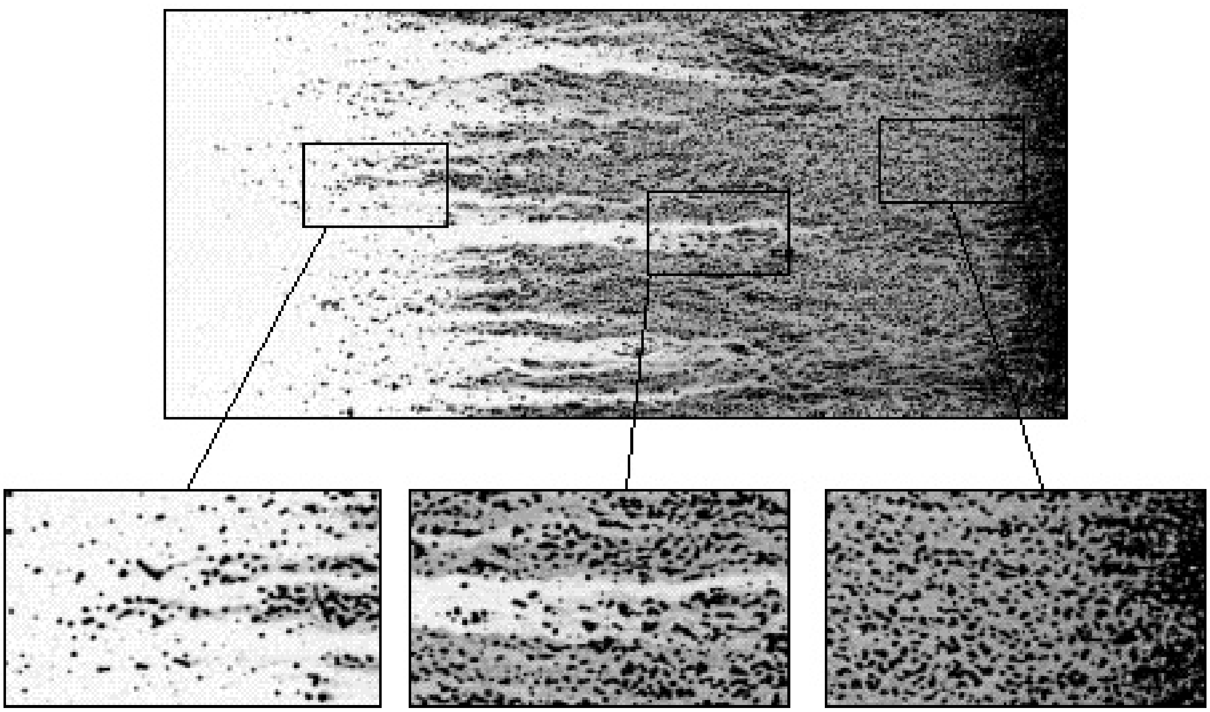
b) TCE after water flood



c) TCE mobilization pure water



d) TCE mobilization surfactant solution



e) Enlargement of full cell and several zones within during dissolution

Figure 8. TCE mobilization and solubilization study in micro-model/fracture. Flow is from left to right in each image of the 15x30 cm micro-model and dark locations are filled with TCE, light with water. a) Final TCE configuration after invading water saturated system, water is entirely entrapped. b) Final TCE configuration after subsequent water flood, TCE is fully entrapped with a large range of blob sizes. Subsequent TCE mobilization with c) high flow rate water flood and d) low IFT surfactant flood. Note the much more pervasive blob structure remaining from surfactant flooding yields a higher TCE saturation for the same capillary number pure water flood. e) After mobilization , TCE dissolves into flowing surfactant fluid exhibiting both dissolution fingering and the formation of a gray macroemulsion. From Zhong et al. (2001).

Macro-heterogeneous media remediation demonstrations:

In Conrad et al. (*in review*), we conducted three bench-scale visualization experiments to remediate TCE from our heterogeneous analog aquifer. Two of these experiments involved surfactants (MA and Tween 80). In the third experiment we injected a potassium permanganate solution to oxidize the TCE. Each remediation experiment benefited from direct collaboration with remedial technology experts. For the MA surfactant flood, we worked with Alex Mayer and Lirong Zhong from Michigan Tech. For the Tween surfactant flood, we worked with Kurt Pennell from Georgia Tech. For the permanganate oxidation, we worked with Jack Istok from Oregon State.

Because we have built realistic hetero structures and we emplaced the TCE in the aquifer by allowing it to migrate as it would as if spilled, we get the TCE to reside in a similar configuration to what we might expect in an aquifer. Here, as in our previous work (Glass et al., 2000, 2001), the majority of the mass is held in high saturation pools. This configuration provided the initial condition for each of our three experiments. In each of these experiments, we have seen that the presence of pools has important implications for remediation success.

In each of the two surfactant experiments, we attempted to recover TCE by solubilization. Addition of a surfactant greatly increases the rate of dissolution, but this comes at a cost. The IFT between the organic phase and aqueous is always significantly reduced. Inadvertent downward mobilization of the DNAPL due to IFT reduction (causing a reduction in the capillary forces holding the DNAPL in place) has long been a concern. Mobilization occurred in both the MA and Tween surfactant floods. In the MA experiment, a more than fifty-fold reduction in IFT resulted in immense mobilization (see figure 9). The most serious consequence was that the considerable reduction in IFT reduced capillary forces to the point that TCE was able to penetrate fine-textured units. As the TCE mobilized it left behind a residual saturation along its migration path. Within the confines of the aquifer, some residual became trapped in fine-textured units. This slowed the solubilization process we had intended to facilitate since surfactant supply to these units is hindered by low permeability. Even more deleterious, however, a significant quantity of TCE penetrated into aquitard at the base of the aquifer, making things far worse than before (see figure10). With regard to TCE recovery, this surfactant flood was not considered a success.

In the Tween experiment, reduction of IFT was not as dramatic and the consequent mobilization, while significant, was much more manageable. Since capillary forces maintained some effect, migration was constrained to pre-existing pathways. TCE did not go into fine-textured regions, and more importantly, it did not penetrate the aquitard. The solubilization process was considered successful, with only a small pool of TCE remaining at the conclusion of the experiment. Figure 11 shows the progress of the solubilization process over time.

From these two experiments, we see that the propensity to mobilize during surfactant flooding was vastly enhanced by the fact that DNAPL was held in pools. And significant mobilization into fine-grained units (especially the aquitard) can make the problem worse. Remember the Hippocratic oath of remediation – first, do no harm. It is from these experiments that we discovered the “capillary bellows” process whereby markedly different IFTs ahead and behind the surfactant front provides a mechanism for mobilization. As the surfactant front comes into contact with a pool the low IFT at the front, a strong capillary pressure gradient forms allowing contraction of the organic/aqueous interface, resulting in mobilization of the contents of the pool as the nonwetting phase is pushed toward the low IFT region, through and behind the surfactant front. This process is discussed in some detail in our paper.

In our third experiment, injection of a potassium permanganate solution resulted in precipitation of MnO_2, a reaction product, creating a low-permeability rind surrounding the DNAPL pools (see figure 12). Formation of this rind hindered contact between the permanganate and the DNAPL, limiting the effectiveness of the remediation. Due to this rind formation, the permanganate

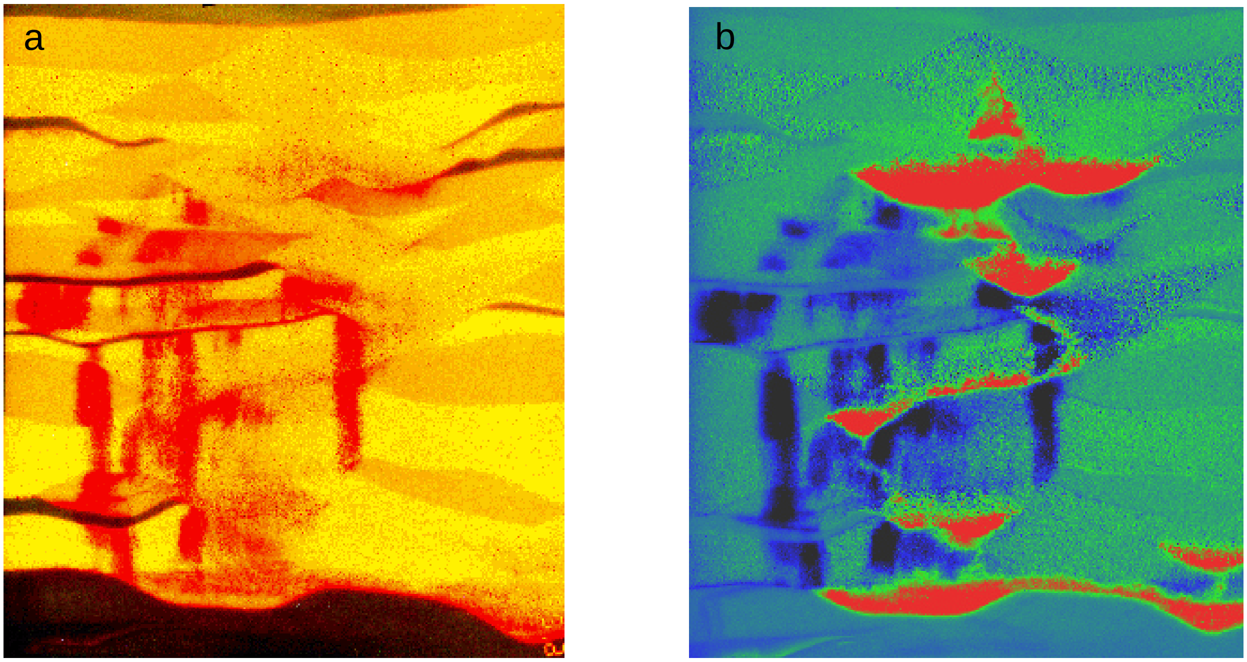


Figure 9. Extent of TCE mobilization after introduction of 2.6 pore volumes of MA surfactant solution (a) photograph showing red-dyed TCE, and (b) processed digital image where red denotes regions where TCE has been mobilized from and black and blue denotes regions where TCE has mobilized to. In the digital image, the red color shows the initial configuration of the TCE in a series of pools. Notice that all the pools have completely drained. Underexposure of the fine sand aquitard at the beneath the lowermost pool prevents us from seeing the extent of migration into the aquitard on these images. Chamber size is 60x60 cm. (Conrad et al., in review)

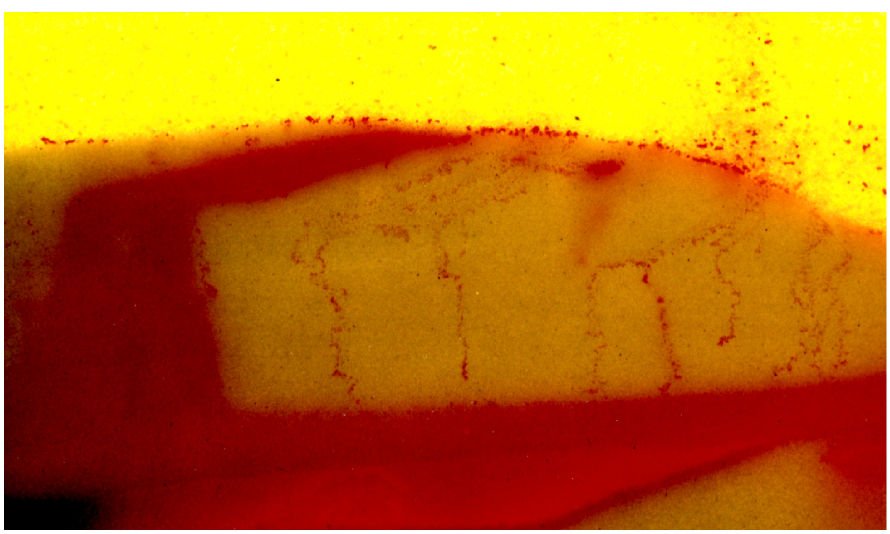


Figure 10. Enlarged photograph of mobilized TCE penetration into the fine sand aquitard during the MA surfactant flood. This photo shows the extreme lower left portion of the chamber and the pervasive penetration of the aquitard with mobilized TCE after 13.6 pore volumes of surfactant flooding. (Conrad et al., in review)

a b

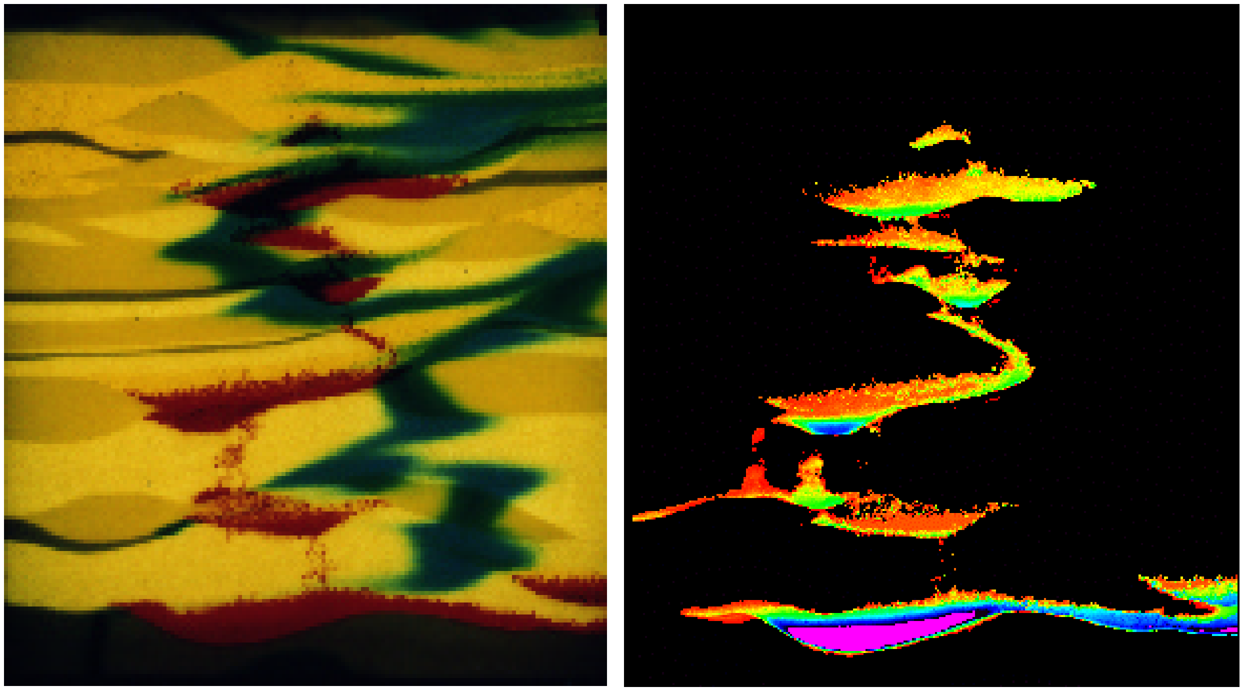


Figure 11. Images summarizing the Tween 80 surfactant flood. (a) Photograph of initial TCE configuration with the blue pulse showing aqueous-phase transport proceeding from left to right. (b) Digital image summarizing the solubilization process. The progression from warm to cool colors denotes the temporal order in which solubilization occurred. The lavender color denotes TCE remaining in the lowermost pool after 8.6 pore volumes at the conclusion of the experiment. Note that comparatively little mobilization has occurred and no penetration of the aquitard. (Conrad et al., in review)

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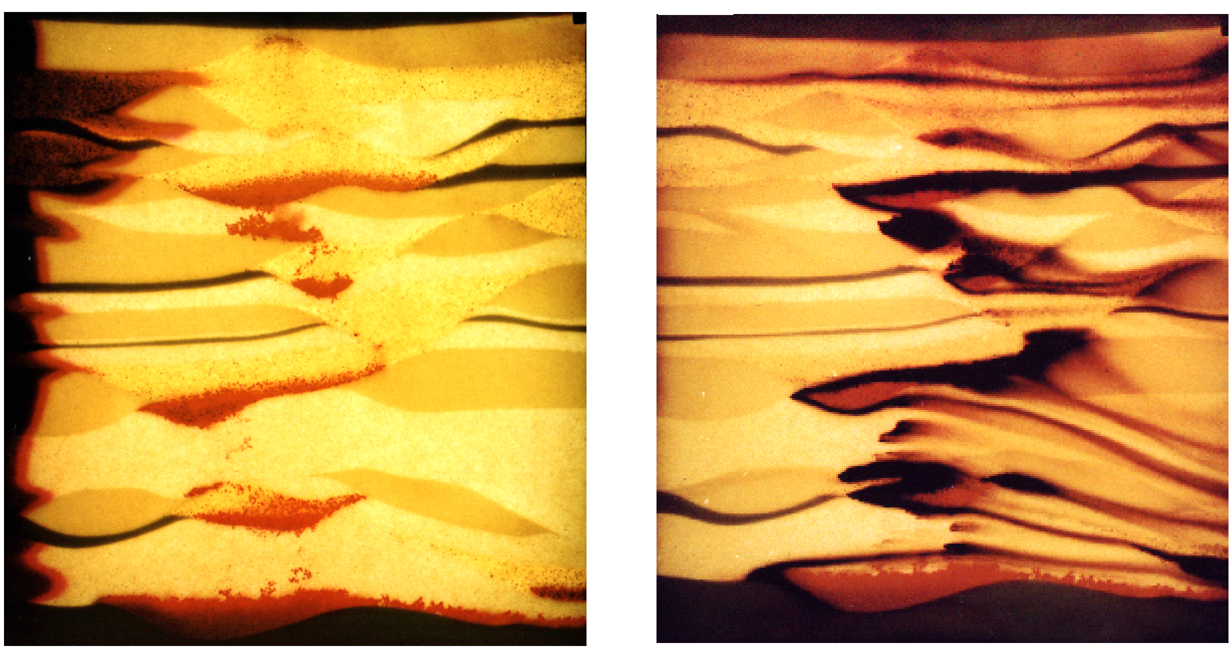


Figure 12. Images from the potassium permanganate oxidation experiment. (a) At the beginning of the experiment, the configuration of the TCE and the invasion of the permanganate solution from the left is seen. (b) At the conclusion of the first permanganate pulse precipitated and suspended MnO_2 reaction product (brown and black) is seen encapsulating the TCE pools, isolating them from further oxidation. (Conrad et al., in review)

experiment was not considered a success. Again, explicit consideration of TCE configured predominantly into pools resulted in the elucidation of a clogging processes that was conjectured but heretofore not substantiated by any other experiments conducted to date.

Our experiments graphically demonstrate that conducting sand tank bench scale experiments of remedial process is a necessary step that must be undertaken prior to pilot scale testing. Visualization is an important component. Building sand tank lithologies evocative of aquifer lithologies is important. Experiments and analyses founded on an assumption of nonwetting phase held predominantly as a residual saturation may have limited applicability to situations where mass is held predominantly in pools. Failure to consider the presence of DNAPLs held in pools during remediation design may lead to decreased performance, inadvertent downward mobilization, or isolation of the TCE from further remediation. Experiments of this type are essential to developing improved understanding of fundamental physics and chemistry controlling remediation processes.

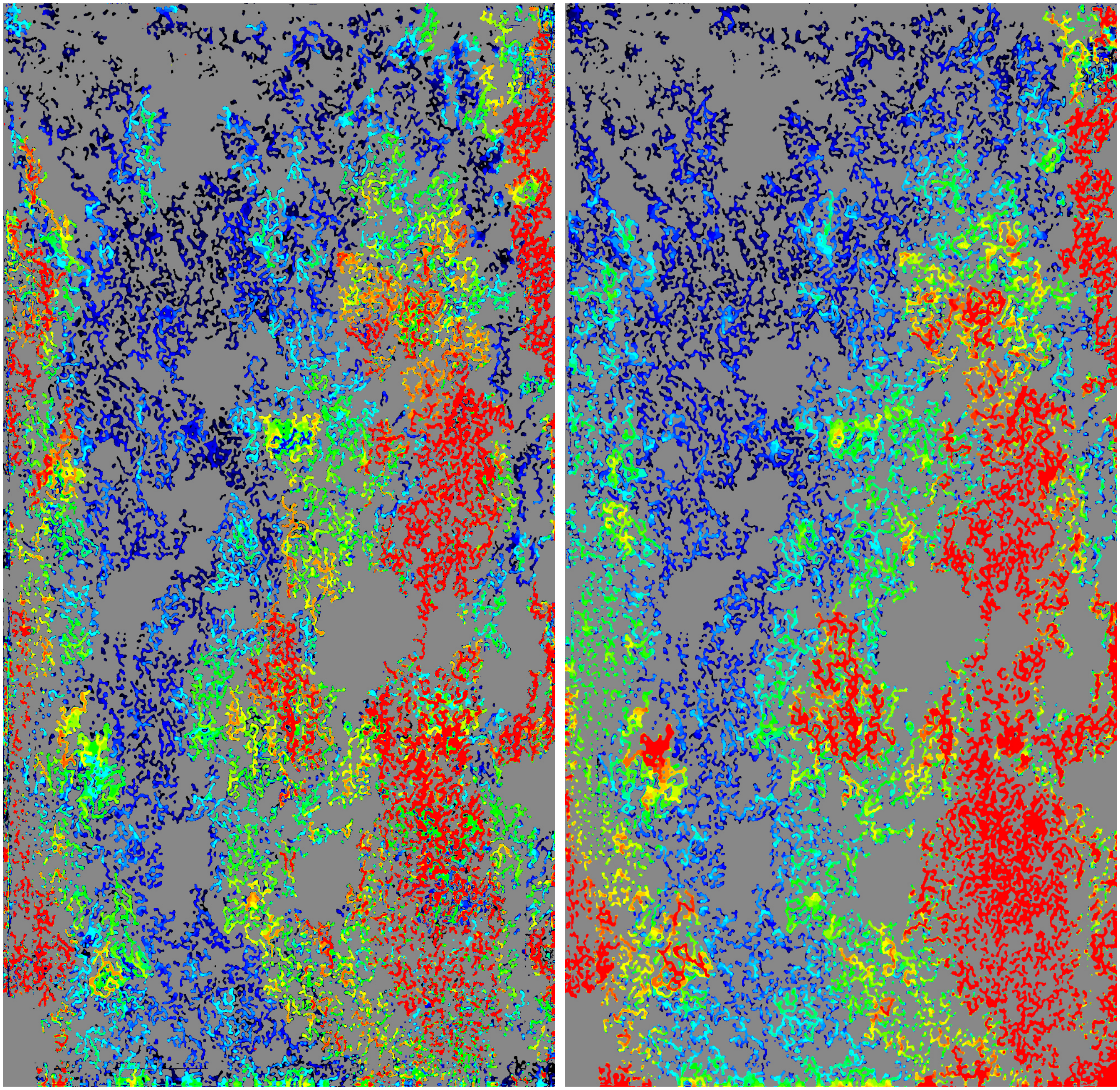
Preliminary Partitioning Interwell Tracer Test (PITT) study in macro-heterogeneous media:

In the process of conducting the remediation demonstration experiments in Conrad et al. (*in review*), we used the opportunity of having TCE configured realistically to run a preliminary partitioning interwell tracer test (PITT). For the PITT, we worked with Varadarajan Dwarakanath from Duke Engineering. A PITT is conducted to characterize the extent of contamination by quantifying the mass of DNAPL present in the subsurface. The PITT consists of injection of a suite of conservative and partitioning tracers with subsequent production of the tracers from a nearby extraction well. The partitioning tracers are more oliophillic and preferentially but reversibly partition into organic phase (i.e., DNAPL) encountered along the flow path. This interaction between the tracer and the DNAPL causes chromatographic separation of the conservative and partitioning tracers. It is from this separation in average travel times between the conservative and partitioning tracers as they travel from injection to extraction well that allows quantification of the DNAPL mass along the swept volume. This method assumes a local equilibrium for interphase partitioning. Consequently, the test must be designed with flow velocities that are slow enough to allow for equilibrium partitioning.

Prior to performing the permanganate experiment, we capitalized on the opportunity of a known quantity of TCE in place in our experimental chamber to perform a PITT under well-controlled conditions. Our preliminary results show that the PITT underpredicted the mass of DNAPL by ~30%. We hypothesize the potential causes for this underprediction may be due to inadvertently violating the assumption of equilibrium partitioning by implicitly assuming DNAPL present as residual blobs rather than predominantly in pools. Standard design practice to date has been to assume DNAPL present as a residual saturation and without much forethought we reverted to standard practice. For this problem, equilibrium is achieved only if diffusion through the organic phase occurs rapidly relative to advective transport of tracers past the organic phase. The characteristic time constant for diffusion is proportional to the distance over which diffusion occurs, or thickness of the organic phase. Of course, blobs are pore-scale features and diffusive processes will achieve equilibrium quickly through blobs relative to pools, which can be 2 to 3 orders of magnitude thicker. Implications for field-scale testing may be that very slow tracer flow velocities may be required to achieve local equilibrium with DNAPL contained in pools.

Current thinking on remediation modeling:

We note that our original intent was to compare our results for the remediation experiments to existing codes using standard two-phase compositional approaches. However, based on what we have seen in our experiments, existing codes will need significant modification before they could be even approximately applied. At this stage, such modeling would not further our understanding of remediation as it would not properly incorporate the dynamics we observe and thus could only be treated as a black box. In related work in fractures funded by *BES Geosciences*, significant progress has been made in the development of fundamental modeling approaches that focus modeling efforts to be the same scale as our lab experiment. There, a MIP model is used to define the migration and dissolution path of individual DNAPL blobs while continuum models are applied to consider flow around and transport from the entrapped DNAPL (Detwiler et al. *accepted*) (see figure 13). A variant of this approach, focused on confronting the issue of mobilization by IFT reducing fluids, must be addressed to properly underpin remediation simulation.



Experimental TCE dissolution **MIP-Continuum dissolution simulation**

Early **Late**

Dissolution Order

Figure 13. TCE Dissolution in flowing fracture, experiment and simulation. We followed the dissolution of TCE entrapped within flowing pure water in the fracture of Zhong et al. (2001) using our quantitative light transmission methods (left). Initial flowing water is shown as gray. We then modeled the dissolution process starting with the initial experimental TCE saturation field using a combination of MIP (Glass et al., 1998) to properly shrink the entrapped TCE and continuum approaches for water flow (Nicholl et al., 1999), transport (Detwiler et al., 2000) and interphase transfer (right). From Detwiler et al. (*accepted*).

Summary and statement of "critical use results" from our research

We have made significant progress in the study of DNAPL migration and remediation in heterogeneous porous media. This progress has resulted from the combination of DNAPL migration visualization within controlled micro-model and heterogeneous porous media systems and the development and application of MIP approaches that model results exceptionally well. Conceptualization of DNAPL migration in a non-continuum, network mode has allowed us to understand process well enough to derive length scales for pool height, pulsation, and finger width within a heterogeneous system. Additionally, it has allowed us to understand the capillary bellows mechanism important in the formation of oil banks and pool drainage within a heterogeneous aquifer during IFT reduction remediation. Remediation experiments have shown both the successes and pitfalls of surfactants and in situ oxidation in the presence of even small pools. As pools are expected at these and larger scales within any aquifer, such remediation methods must be used with caution. Ours are the first experiments that we are aware of that demonstrate the significant mobilization possible when pools are present. All other research has been conducted in near homogeneous tanks and columns or in the presence of very simple heterogeneity structure.

Distilling from our research outlined above, we believe the following "products" and increased understanding to be of immediate and critical use to DOE DNAPL spill sites and cleanup efforts:

1. A fundamentally new and physically correct model (MIP) for DNAPL migration has been formulated, implemented and tested. This model can be extended to include the contact angle aging process found in mixed DNAPLs and combined with miscible transport codes to model DNAPL mobilization on IFT lowering and subsequent solubilization.

2. A series of length scales for DNAPL structure (i.e., pool height, finger diameter, and pulsation location) have been derived as a function of capillary, gravity and viscous forces within a heterogeneous media. These length scales can be combined to form the basis of a large scale structural growth model for DNAPL migration as well as the design of remediation applications.

3. The importance of heterogeneity to cause saturations much higher than residual throughout an aquifer has been clearly demonstrated. This multiple scale pool structure will largely control DNAPL migration extent and critically influence remediation attempts. Both DNAPL delineation before remediation and remediation design must be accomplished with this critical structure in mind.

Most importantly, *we emphasize caution and advocate a restrained approach to site remediation at this time*. In all cases considered so far, the initial configuration of the DNAPL dramatically influenced the efficacy of the remediation method. Pools, expected at all scales from those in our experiment up to 10's of meters, are expected within an aquifer. Use of surfactants that cause excessive IFT reduction can cause the downward mobilization of the DNAPL and its penetration of low permeability layers. Such a scenario may have already happened at Portsmouth where a surfactant pilot test with MA was performed and subsequent characterization has found the shale forming the bottom of the aquifer to be penetrated with TCE within its top foot (Doug LaBrecque, Steamtech, personal communication). Since full recovery of surfactant is never achieved, the migration of this fluid down gradient will continue to mobilize DNAPL far outside of the region where it was originally used. In situ oxidizers do not mobilize DNAPL; however, they build a low permeability rind around all the pools, isolating them from future oxidation. *Thus, all of these remediation approaches must be carefully considered prior to field implementation so that an existing contamination situation is not made worse.*

Emphasis of Future Research

We have found that liquid phase DNAPL movement in the context of heterogeneities, initially, during redistribution, and subsequently mobilized in the presence of characterization and remediation fluids is the critical determiner of remediation success or failure. Therefore, future research should be focused on liquid phase movement in the context of heterogeneity with a lower priority placed on the consideration of DNAPL removal due to subsequent solubilization or oxidation. If during remediation, we can keep the DNAPL from mobilizing to where we can't get at it, then we believe remediation schemes can be optimized to remove it. For example, consider the reasonable success of the Tween 80 experiment (described above). Therefore, we must understand and constrain mobilization within the heterogeneous system so that remediation can first do no harm. Since mobilization is brought on by IFT reduction (through the introduction of surfactants or alcohols) and since these remain among the most promising remedial techniques, future research should be focused toward their continued study. Additionally, the issue of so-called "dirty DNAPLs" -- less ideal, more realistic multi-component organic liquids as well as other remediation techniques such as air sparging should be investigated in the context of heterogeneous aquifers.

As in our research effort outlined above, we believe a research approach combining both experiments and modeling will most effectively yield the understanding required for DNAPL problem solution. Experiments should build on our experience gained in the past 3 years, and in particular should extend our preliminary work considering the effect of micro-heterogeneities such as laminations and crossbedding. Modeling should build on the MIP approach with the implementation of a set of new feature to handle contact angle dynamics and local viscous forces, as well as the combination of MIP with continuum approaches for the removal of dissolved DNAPL or remedial agents within the water phase.

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